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ADSORPTION OF TRACE ELEMENTS FROM SEAWATER BY CHELEX 100

by

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ABSTRACT

Chelex 100 was evaluated as an ion-exchange resin for the extraction of trace elements from seawater. A modification of the limited bath technique was used, in which resin was added to a solution containing the trace element. After time for equilibration, the solution was analyzed and the fraction of the activity adsorbed by the resin was determined.

Chelex 100 appears to be an excellent ion-exchanger for extracting a number of trace elements from seawater. These include: Ni, Zn, Ce, La, Tm, Pb, Am, Tb, Mn, Bi, Pu, Cr, Th, Co, Cd, Fe, and Hg.

SUMMARY

Problem

The purpose of this investigation was to determine the feasibility of using Chelex 100 chelating ion-exchange resin for the concentration of trace elements from seawater. This is the first step in the development of an *in situ* system for rapidly concentrating radioactivity in the ocean, a system required for the monitoring of ocean areas for radioactive materials.

Findings

The adsorption on Chelex 100 of thirty-seven elements was determined. Seventeen of these elements were strongly adsorbed ($\log D > 3$ or > 90 % adsorption): Ni, Zn, Ce, La, Tm, Pb, Am, Tb, Mn, Bi, Pu, Cr, Th, Co, Cd, Fe and Hg. Another five were moderately adsorbed ($\log D =$ 1.9-3 or 50-90 % adsorption): Sn, Ru, Zr, Nb and Ba. The remaining fifteen were relatively weakly adsorbed ($\log D < 1.9$ or < 50 % adsorption): Ag, Ga, Sr, Ca, Sc, Tl, Tc, Ta, Te, Sb, Ge, Cs, Na, Se and Mo. The preliminary basis for the desired *in situ* concentration system thus exists.

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INTRODUCTION

A program for the development of an in situ system for rapidly concentrating and identifying radioactivity in the ocean has been established at this Laboratory.

Such a system is required for the monitoring of ocean areas for radioactive materials.

The first and most important phase of this program is the selection of a method for the concentration of trace amounts of radionuclides from seawater. Some of the requirements for such a concentration method include: rapid concentration of the trace elements from relatively large volumes of seawater (~1000 liters); adaptability and construction of a rugged, reliable system that can be operated from shipboard; and adaptability to in situ operation at depths to several thousand meters.

The present investigation has centered around the use of an ion-exchange concentration system based on Chelex 100 chelating ion-exchange resin. This report describes the behavior of this resin with seawater-compatible states of 37 elements, which include fission products, neutron-induced radionuclide activities of seawater, naturally occurring radionuclides in seawater, and other radionuclides that were conveniently available at this Laboratory.

Objective

This investigation was intended as a brief survey for determination of the feasibility of using Chelex 100 in the concentration of trace amounts of radionuclide activity from seawater. It was not intended to be a definitive study for determination of optimum parameters for the adsorption process, nor was it the purpose to determine the kinetics or mechanisms of the adsorption reactions. If the results of this preliminary survey proved encouraging, a more extensive study of the resin system could later be conducted.

Background

Chelex 100, a processed form of Dowex Resin 1A, is a chelating ion-exchange resin which has an unusually high preference for copper, cobalt, and other heavy metals over such cations as sodium, potassium, magnesium and calcium. Since these latter cations, which constitute more than 99.9 % of the total cationic constituents of seawater,[1] are not retained by the resin, Chelex 100 seemed to be a promising material for extraction of the other components of seawater.

Initial Chelex-100 studies conducted at NRDL with cobalt[2,3] and plutonium[4] isotopes indicated that these cations can be efficiently removed from seawater. The reported[5] approximate order for cation retention by Chelex 100 in chloride medium is $Cu^{+2} \gg Pb^{+2} > Al^{+3} > Cr^{+3} > Ni^{+2} > Zn^{+2} > Ag^{+1} > Co^{+2} > Cd^{+2} > Fe^{+2} > Mn^{+2} > Ba^{+2} > Ca^{+2} > Na^{+1}$.

Approach

The experimental work was conducted in two phases:

Phase I: Preliminary Experiments with Ce^{144} Tracer. These preliminary experiments were conducted for guidance in the establishment of experimental conditions for the following Phase II experiments. The conditions studied included the weight of resin to be used per unit volume of seawater and the time of stirring necessary for establishment of equilibrium between the resin and Ce^{144}. It was understood by the authors that optimum conditions selected for the Ce^{144} system might not necessarily represent optimum conditions for other nuclides. Ce^{144} was selected because it was one of the more important gamma-emitting fission product activities that would be studied in detail at a later date.

Phase II: Determination of log D (the base 10 logarithm of the distribution coefficient) for other radionuclides under the conditions established for Ce^{144} adsorption.

EXPERIMENTAL

Materials

1. Resin: 50-100 mesh Chelex 100, a chelating ion-exchange resin, produced by Bio-Rad Laboratories, Richmond, California.

2. Seawater: Natural Pacific Coast seawater, salinity 35 $^{o}/_{oo}$, filtered through a 0.45-μ membrane filter (Millipore) just prior to use.

3. Radioactive tracers: Obtained from either the Isotopes Division of Oak Ridge National Laboratory or the Nuclear Science and Engineering Corporation. Some of the tracers contained inert carrier. In such cases the quantity of carrier introduced into the test solution was limited so that the final concentration of the element was 10^{-8} M.

Phase I. Preliminary Experiments with Cerium-144 Tracer.

Rates of adsorption of Ce^{144} (added in the +3 oxidation state) on varying weight fractions of Chelex 100 and for different stirring times were determined with a modification of the limited bath technique.[6] Fifty ml of a seawater solution containing Ce^{144}, with about 10^{-8} M cerium carrier in all cases, were placed in a 100-ml beaker and stirred at a constant rapid rate at 25°C. A quantity of resin was then rapidly added. After the desired time interval, the mixture was centrifuged. A suitable aliquot of the supernate was analyzed by gross gamma counting for determination, by difference, of the extent of the Ce^{144} adsorption.

Figure 1 shows the adsorption of Ce in seawater at 25°C as a function of time for three different weight fractions of Chelex 100. The results indicated that the rate of adsorption, for any given weight fraction of resin, was very rapid initially and then decreased with time, approaching complete adsorption asymptotically. Rates of individual radionuclides depend on the quantity of resin in contact with the solution. Equilibrium for cerium was reached within 60 minutes with 0.2 g of Chelex 100 (resin/seawater = 4.0 mg/ml) and within 30 minutes when 0.34 g of Chelex 100 (resin/seawater = 6.8 mg/ml) were used.

Phase II. Determination of log D for 37 Elements.

The experimental procedure used in Phase II was derived from that developed in Phase I. However, some modification of the original procedure was made to provide more favorable conditions for the establishment of equilibrium.

To a 50-ml polyethylene centrifuge tube were added 0.25 g of Chelex 100 and 20 ml of natural seawater solution (resin/seawater = 12.5 mg/ml) containing the individual radioactive tracer. No attempt was made to adjust the oxidation states of the tracers in seawater. The oxidation states given were for the tracers before addition to seawater. These were the expected states in seawater. The solution was stirred vigorously with an overhead stirrer for an hour. After centrifugation, aliquots were counted in a gamma well-counter or pulse-height spectrometer (for gamma-emitting isotopes) or in a liquid scintillation counter (for alpha- or beta-emitting isotopes).

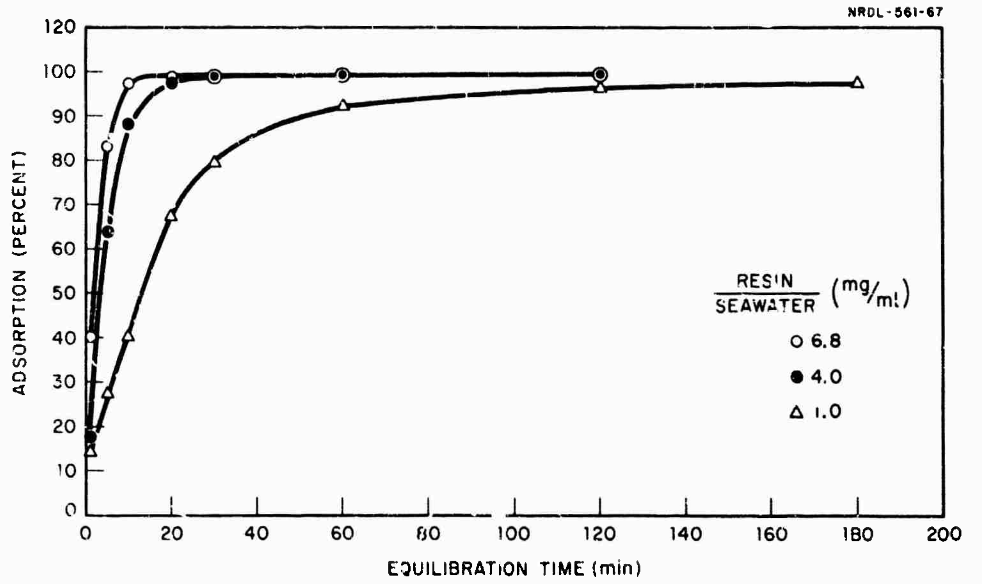

Fig. 1 Rate of Adsorption of Cerium on Chelex 100.

The results are expressed in terms of the logarithm of the distribution coefficient ($\log_{10} D$). The distribution coefficient, D, is defined as the ratio of the amount of metal ion adsorbed per gram of exchanger to the amount of metal ion per milliliter of contacting equilibrium solution. For the conditions of the present experiments

$$D = 80 \frac{C_b - C_a}{C_a}$$

where: C_b = counts of tracer or amount of element per milliliter before equilibrium.

C_a = counts of tracer or amount of element per milliliter after equilibrium.

The percentage adsorption is given by

$$\% \text{ Adsorption} = 100 \frac{C_b - C_a}{C_b}$$

$$= 100 \left(\frac{D}{D+80}\right)$$

Results

The results of the adsorption of the trace elements on Chelex 100 are presented in Table 1.

DISCUSSION

The order for cation retention by Chelex 100 in seawater listed in the Table is generally in agreement with that reported in Reference 5 for chloride medium (see Introduction). There was some rearrangement in the order of the elements with large log D, 3.5-4.9 (97.2 % - 99.7 % adsorption by resin phase). The only significant difference, however, was for Ag. Ag retention reported in chloride medium[5] was higher than

TABLE 1

The Adsorption Characteristics of Trace Elements on Chelex 100

Tracer*	Adsorption (%)	Log D
Ni^{63} (II)	99.9	4.90
Zn^{65} (II)	99.9	4.90
Ce^{144} (III)	99.8	4.60
La^{140} (III)	99.6	4.33
Tm^{170} (III)	99.5	4.20
Pb^{210} (II)	99.4	4.11
Am^{241} (III)	99.4	4.11
Tb^{160} (III)	99.0	3.90
Mn^{54} (II)	98.4	3.69
Bi^{207} (III)	97.9	3.57
Pu^{238} (IV)	97.5	3.49
Cr^{51} (III)	97.2	3.45
Th^{230} (IV)	96.5	3.34
Co^{60} (II)	96.5	3.34
Cd^{109} (II)	96.4	3.32
Fe^{59} (III)	95.0	3.18
Hg^{197} (II)	92.2	2.97
Sn^{113} (IV)	80.8	2.53
Ru^{103} (III)	63.1	2.15
Zr^{95} (IV)-Nb^{95} (IV)	59.2	2.06
Ba^{140} (II)	49.3	1.89
Ag^{110m} (I)	43.3	1.79
Ga^{68} (III)	39.5	1.72

Continued

TABLE 1 (Cont'd)

The Adsorption Characteristics of Trace Elements on Chelex 100

Tracer*	Adsorption (%)	Log D
Sr^{85} (II)	39.1	1.71
Ca^{45} (II)	38.4	1.70
Sc^{44} (III)	27.8	1.50
Ti^{44} (IV)	23.4	1.40
Tc^{95} (VII)	21.1	1.34
Ta^{182} (V)	12.2	1.08
Te^{131} (IV)	4.2	0.54
Sb^{124} (III)	3.1	0.42
Ge^{68} (IV)	2.0	0.20
Cs^{137} (I)	1.9	0.18
Na^{22} (I)	0.6	-0.3
Se^{75} (IV)	0.6	-0.3
Mo^{99} (IV)	0.6	-0.3

*The oxidation states given are for the tracer before addition to seawater.

that of Co, Cd and Fe. However, in the present seawater study its log D was 1.79 (43.3 % adsorption) as against 3.34 (96.5 % adsorption), 3.32 (96.4 % adsorption) and 3.18 (95 % adsorption) for Co, Cd and Fe, respectively.

Several generalizations may be made to explain the differences between the two listed orders. These include (1) differences in oxidation states of the various trace elements in the two media, (2) differences in kind and extent of complex ion formation and (3) differences in pH and composition of the two solutions.

Of the 37 isotopic elements surveyed, 17 elements had log D of 3 or greater (> 90 % adsorption by the resin) and 5 had log D between 1.0-3 (50-90 % adsorption). Since many of these isotopes were processed in other-than-optimum conditions (particularly of pH) the log D could conceivably be improved.

CONCLUSION

The use of Chelex 100 as an ion-exchanger for the concentration of trace elements from seawater appears to be very promising. The resin has a particularly high affinity for Ni, Zn, Pb and several of the actinides and lanthanides (including the high yield fission products La^{140} and $Ce^{141,144}$).

The method of concentrating the trace elements from seawater is simple and should be readily adaptable to the rapid and if necessary <u>in situ</u> processing of relatively large volumes of seawater.[7]

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